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## Investigation of the Properties of Unsaturated Allyl Alcohol and its Oxidation Reaction Products

### Abstract

Organic substances in which the -OH group is directly attached to the carbon atom are called alcohols. Unsaturated alcohols are obtained by replacing the hydrogen of ethylene or acetylene-type compounds with a hydroxyl group. Allyl alcohol, the first representative of the class of unsaturated alcohols, contains oxygen. Allyl alcohol is used in optical resins, protective glasses, paints and coatings and polymer cross-linking agents, as well as in the production of pharmaceuticals, organic chemicals, plastics, herbicides, and pesticides. In organic chemistry, alcohols can be oxidized to aldehydes, ketones, carboxylic acids, and esters that carry a higher oxidation state of carbon. Therefore, the selective oxidation of alcohols is an important issue. The properties and selective oxidation reaction of allyl alcohol were investigated in the presented work.

**Keywords:** *unsaturated alcohols, allyl, properties, selective oxidation, acrylic acid*

### Introduction

Alcohols are organic substances in which the -OH group is directly attached to a carbon atom. According to the nature of the hydrocarbon radical, they are classified into saturated, unsaturated and aromatic alcohols.



## Research

Organic compounds consisting of one or more hydroxyl groups combined with a radical of saturated hydrocarbons in the molecule are called saturated alcohols (Dashdamirov, 2017). Unsaturated alcohols are obtained by replacing the hydrogen of ethylene or acetylene-type compounds with a hydroxyl group. Esters of vinyl alcohols are very valuable raw materials in polymer chemistry (Selda, 2003). For example; Allyl alcohol ( $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ ), a foul-smelling liquid contained in garlic, is used in the production of ether synthetic resin with phthalic acid. In nature, unsaturated alcohols with higher carbon numbers are found in vegetable oils. These are called isoprene-type compounds. Because they exist as dimers, trimers and tetramers of isoprene (Selda, 2003).

According to the number of hydroxyl group (OH), saturated alcohols are monoatomic ( $\text{C}_n\text{H}_{2n+1}\text{OH}$ ), diatomic ( $\text{C}_n\text{H}_{2n}(\text{OH})_2$ ), triatomic ( $\text{C}_n\text{H}_{2n-1}(\text{OH})_3$ ) and so on. The polarity of the hydroxyl group and its hydrogen bond formation is an important physical property of alcohols. As a result, they dissolve well in water by boiling at high temperatures (Dashdamirov, 2017).

### Unsaturated Alcohol Allyl, its Preparation and Properties

Allyl alcohol, the first representative of the class of unsaturated alcohols, contains oxygen. Allyl alcohol can also be called Vinylcarbinol, 2-Propenyl alcohol, 3-Hydroxypropene, 2-Propenol, allylic alcohol, 1-Propen-3-ol, Propenyl alcohol. It is a colorless liquid with a pungent, mustard-like odor. It is soluble in water as well as in many organic solvents. It is miscible with water in all proportions and forms an azeotropic mixture (28.3 %  $\text{H}_2\text{O}$ ) and its chemical structure is  $\text{CH}_2\text{CHCH}_2\text{OH}$ . It is very toxic and dangerous for the environment. It is a transparent liquid with a molecular mass of 58.1, a melting point of  $-129^\circ\text{C}$  and a boiling point of  $97^\circ\text{C}$ . Allyl alcohol can be obtained by the following methods.

1. From the hydrolysis of allyl chloride.
2. From the isomerization of propylene oxide.
3. From the dehydrogenation of propanol-1.
4. From the reaction of glycerin with formic acid.
5. From the oxoacylation of propylene to allylacetate.

Despite environmental concerns, allyl alcohol is an important organic intermediate in the synthesis of polymeric compounds produced industrially from petroleum-derived propylene. It is an industrially important olefinic alcohol, it can be used as a raw material or precursor for many chemicals. It is raw material for the synthesis of various allylic derivatives like allyl diglycol carbonate, allyl glycidyl ether, 1,4-butanediol, polystyrene-allyl alcohol, etc. When allyl alcohol is treated with concentrated HCl at  $100^\circ\text{C}$  in the presence of  $\text{ZnCl}_2$  or at  $200^\circ\text{C}$  in the presence of  $\text{CuCl}_2$ , it turns into allyl chloride, and when passed over  $\text{Al}_2\text{O}_3$  at  $200-300^\circ\text{C}$ , diallyl ether is obtained. Simple and complex esters are easily obtained from allyl alcohol. The conversion of allyl alcohol to acrolein occurs by alcohol dehydrogenase. Allyl alcohol is used in optical resins, protective glasses, paints and coatings, silane coupling agents, and polymer cross-linking agents. It is also used in the production of pharmaceuticals, organic chemicals, plastics, herbicides and pesticides. Before handling allyl alcohol, workers should be trained in proper safe handling and storage procedures (Shashkova, Mezhuev, & Tsatsakis, 2024; Aliahmadi, Kharat, & Janczak, 2024; Sawant & Mehendale, 2005).

### Oxidation of Allyl Alcohol

In recent decades, a number of reagents and methods have been developed for the oxidation of alcohols to carbonyl compounds. In organic chemistry, alcohols can be oxidized to aldehydes, ketones, carboxylic acids, and esters that carry a higher oxidation state of carbon.

*Oxidation of Allyl Alcohol to Acrolein:*  $\text{C}_3\text{H}_5\text{OH} + [\text{O}] \rightarrow \text{C}_3\text{H}_4\text{O} + \text{H}_2\text{O}$

The subsequent oxidation of acrolein ( $\text{C}_3\text{H}_4\text{O}$ ) leads to the formation of acrylic acid ( $\text{C}_3\text{H}_4\text{O}_2$ ).

*Oxidation of Acrolein to Acrylic Acid:*  $\text{C}_3\text{H}_4\text{O} + [\text{O}] \rightarrow \text{C}_3\text{H}_4\text{O}_2$

*Overall Reaction Sequence:*  $\text{C}_3\text{H}_5\text{OH} + 2[\text{O}] \rightarrow \text{C}_3\text{H}_4\text{O}_2 + \text{H}_2\text{O}$

Recent experimental and theoretical studies have been presented on the mechanisms of formation of oxygen-containing active sites on the silver surface and their participation in the

oxidation of alcohols to carbonyl compounds, as well as in the conversion to new Ag-containing catalytic composites (Vodyankina, 2022).

The move towards the production of more sustainable and greener chemicals requires the development of new synthetic materials and processes that offer enhanced atom economy and energy efficiency. In this regard, the oxidation of the corresponding alcohol derivatives, which offers a low temperature, cost-effective and clean approach, has wide applications in the agrochemical, fragrance/flavor and pharmaceutical sectors, as the green synthesis of allyl aldehydes, an important class of multifunctional chemical intermediates, has been the focus of intensive academic and commercial research due to its selectivity. Using highly organized mesoporous alumina produced by Evaporation-induced self-assembly (EISA) synthesis as a support for Pd nanoparticles Atom-efficient, aerobic oxidation of allyl alcohols to aldehydes/ketones under mild reaction conditions gives active and highly selective catalysts (Parlett et al., 2013).

Allyl alcohol molecularly adsorbs and desorbs from the pure Au(111) surface without undergoing any chemical transformation. Oxidation of allyl alcohol to acrolein occurs on oxygen-covered Au(111) surfaces via a mechanism similar to that proposed for other alcohol species over gold catalysts: dehydrogenation of the hydroxyl hydrogen to form alkoxide on the surface, followed by  $\alpha$ -dehydrogenation of the alkoxide to selectively form the aldehyde product. The oxidation of allyl alcohol to acrolein occurs via three distinct reaction pathways on the Au(111) surface, dictated by the relative populations of atomic oxygen and hydroxyl species on the surface. Similar results were not observed in the TPD (Utilizing temperature-programmed desorption) spectra for the oxidation of simple alcohols on the Au(111) surface, which may indicate that allyl alcohols and simple alcohols react differently with the presence of different pores on the surface or that aldehydes are formed on the surface during oxidation (Mullen et al., 2014). It was studied that E- and Z-allylic alcohols (E- and Z-allylic) become stereoconvergent to E-a,b – unsaturated aldehydes (Könning et al., 2014).

The kinetics of oxidation of allyl alcohol with quinaldinium chlorochromate is studied in 40 % acetic acid – water (v/v) medium. According to the concentration of oxidizing and hydrogen ions, the order is one. It is fractional according to the substrate. Increasing the ionic strength has little effect on the rate of the reaction. The reaction does not lead to the polymerization of acrylonitrile (Sekar & Palanivel, 2012).

In the presence of copper (I) chloride, tert-butyl 1-hydroxy-2-methyl-6-trifluoromethyl-1H-indole-3-carboxylate acted as a catalyst for the chemoselective aerobic oxidation of allyl and benzyl alcohols. Various primary and secondary allyl and benzyl alcohols were oxidized to the corresponding a,b – unsaturated carbonyl compounds in good yield without affecting non-allylic alcohols (Shen et al., 2012).

Selective oxidation is very important in synthesis. Here, we reported a Pd-catalyzed method to selectively oxidize allylic alcohols to enones and enals at room temperature. 27 compounds, including enones and enals, were obtained in moderate to excellent yields (Zhang, Li, & Gao, 2022).

Acrylic acid, an important chemical with various downstream applications, is currently produced from petroleum. A new way of producing acrylic acid using a more sustainable and environmentally friendly method, especially starting from biomass-derived glycerol, is being actively pursued. In this study, the selective oxidation of allyl alcohol to acrylic acid, which can be obtained from glycerol with >99 % efficiency without a catalyst, using only water, allyl alcohol, and a catalyst under pressurized oxygen conditions was investigated. Among various metal catalysts, Pd showed the highest activity for acrylic acid production. Oxidation, hydration and hydrogenation pathways were observed simultaneously. When Pd nanoparticle catalysts were used, the starch-coated catalyst produced less hydrogenated propanal and propionic acid species with high yields for acrylic acid. The effect of reaction temperature, oxygen pressure, amount of reactant and catalyst was evaluated (Kim & Lee, 2017).

## Conclusion

Despite environmental concerns, allyl alcohol is an important organic intermediate in the synthesis of polymeric compounds produced industrially from petroleum-derived propylene. At the same time, acrylic acid, which is a product of selective oxidation, is one of the most important monomers in the industry. Acrylic acid and its complex esters are used in the production of acrylic fibers, lacquer coatings, glues, paints, textile auxiliary materials, paper and leather industry. It is used in the production of plastic masses, coating materials, varnishes, copolymers with various monomers, typographic colors, acrylic rubbers, fibers, water-soluble polymers, glues, as well as in the preparation of coatings for the preservation of soil structure in agriculture and preparation of coatings for the storage of medicinal preparations in medicine. Thus, the process of selective oxidation of allyl alcohol for the production of acrylic acid is one of the most important issues.

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